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TECHNICAL REPORT NO. 18

Method of Evaluating the Thermal Stability of the
Pyroelectric Properties of Polyvinylidene Fluoride
Effects of Poling Temperature and Field

by

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Method of Evaluating the Thermal Stability of the Pyroelectric
Properties of Polyvinylidene Fluoride—Effects of Poling Temperature and Field

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Abstract

→ The ac pyroelectric response of a number of differently poled polyvinylidene fluoride films has been measured while the temperature was varied at a constant rate of ^{about} $\times 5$ °C/min. from room temperature to near the melting temperature. The response first increases with increasing temperature which is attributed to an increase of the thermal expansion coefficient and eventually decreases due to melting and/or loss of electric dipole orientation. The details of the temperature dependence are influenced in a reproducible manner by the poling variables especially the poling temperature. The measurement is therefore proposed as a way of evaluating the effect of processing variables on the thermal stability of the piezo and pyroelectric properties. ↗

Introduction

Considerable attention has been devoted in the past decade [1] to the study of the piezo- and pyroelectric properties of polyvinylidene fluoride (PVDF or PVF₂) because of its favorable properties as a transducer component material. The unique properties of PVF₂ transducers include low density, high voltage output, low acoustic impedance, wide bandwidth, flexibility, toughness and ease of fabrication into complex patterns and arrays [2,3]. These properties are ideally suited to yield a great variety of designs for sensors and actuators in many different fields of application [4,5,6] at potentially low cost. A large part of the published literature already reviewed [7,8,9] has been devoted to studies of the structure and processing of PVF₂ films in order to understand the origin of their piezo- and pyroelectric properties and to the construction and evaluation of devices.

Data on the aging and thermal stability of piezo- and pyroelectric properties in polymer films have been reported [10-13]. The temperature dependence of the pyroelectric response [14,15] and of various piezoelectric coefficients and elastic moduli [10,11,16] have also been investigated. Thermally stimulated current (TSC) measurements have been reported [17-20] but these tend to include large currents of electrochemical origin. In general, both the temperature dependence and the long term isothermal aging data on the piezo- or pyroelectric activity show excellent inherent durability of the piezo- and pyroelectric properties of PVF₂ films. Effects of contaminants, mechanical fatigue and other environmental or use conditions are not well known nor is there a good understanding of the physical and chemical mechanisms involved in aging of PVF₂ films.

To aid in our understanding of piezo- and pyroelectric stability we

wanted a rapid measurement method which would give a comparison of the relative thermal stability of samples prepared under different conditions (e.g. poling temperatures, times, fields, draw ratios, etc.). A measurement of piezoelectric response and dynamic modulus during the gradual heating of polymers has shown the effectiveness of such a technique for obtaining information about the relative stability of the polarization responsible for piezoelectricity [10,11]. The method we chose was to measure the ac pyroelectric response while a specimen film is heated by an oil bath at a constant rate from room temperature to the melting point ($\sim 170^\circ\text{C}$ for PVF_2). To induce an ac pyroelectric current and to separate it from depolarization and electrochemical currents, we superimposed on the specimen the heat from a chopped light source on that supplied by the bath heaters and measured the oscillatory part of the current having a frequency equal to the chopper frequency. The data obtained from this measurement are in form of curves of the rms amplitude of the ac electrical response vs. the sample temperature. The value of these curves in ranking different specimens is analyzed in the Discussion section.

The type of measurement described here is reminiscent of the ASTM test of heat distortion temperature (ANSI/ASTM D648) or deflection temperature (ANSI/ASTM D1637) where the temperature of significant decrease of desirable mechanical properties is determined by monitoring the property while the temperature is increased linearly with time. This type of test gives a rough measure of a material's useful temperature range. The data are useful for device design and material optimization and can guide the more careful characterization measurements needed to determine the basic mechanisms of aging.

In this paper we present details of our method which has been improved since our earlier report [15] and show results for PVF_2 samples poled with the same field but at different temperatures, and with different fields at ambient temperature.

Sample Preparation

The samples used in this study were 25 μm thick, biaxially drawn, capacitor-grade PVF_2 films manufactured by the Kureha Chemical Industry Co. Ltd. [21]. Thin film aluminum electrodes, 100 nm thick, were deposited on opposite surfaces of the samples by evaporation under vacuum over a circular area 1.24 cm in diameter. Electrode extensions in the form of tabs were provided for electrical contact outside the circular electrodes.

Nominally identical samples were poled at different maximum poling temperatures, T_p , of 29, 57, 83 and 109 $^{\circ}\text{C}$ respectively, but otherwise received similar treatment. The poling was done in a press with platens fitted with electrical resistance heaters and cooling coils. The samples were sandwiched between 3 mm thick polytetrafluoroethylene sheets along with tin foil electrical leads and a thermocouple which was placed close to the samples. The poling treatment consisted of applying a selected constant voltage across the samples through the tin foil leads while the temperature measured by the thermocouple was made to go through a micro-processor-controlled cycle. This cycle consisted of three consecutive 15-minute time intervals during which the temperature first was increased linearly from ambient to T_p , then was held constant at T_p , and finally was decreased linearly from T_p to ambient. The poling field was maintained for the entire cycle. Twelve of the samples were poled under a mean field E_p of 1 MV/cm (the poling voltage divided by the sample thickness). A few additional samples were poled at room temperature under higher fields of 1.6, 2, and 2.8 MV/cm. In some instances, pairs of samples were poled simultaneously while connected in parallel electrically. This was done to obtain samples with as identical as possible poling history for use in evaluating the reproducibility of the pyroelectric response vs. temperature data among initially similar

samples when these are subjected to similar depolarizing temperature sweeps.

After poling, each sample was mounted in close fitting double hoops which maintained the sample taut and prevented its shrinkage during thermal depolarization. The effects of tension variations were not studied. However, the general features of the temperature dependence were similar to those in our earlier work [15] where the samples were stressfree.

Prior to the depolarization runs, the room temperature pyroelectric coefficient of each of the mounted samples was determined by a previously described method [22]. In this method, the sample is placed inside and in intimate contact with a massive copper cell which can be heated or cooled slowly by the controlled circulation of warm or chilled water through passages in its base. The pyroelectric coefficient is calculated by dividing the current density by the corresponding rate of temperature change. In these measurements, the temperature excursions from ambient are limited to ± 2 K. Data from positive and negative temperature excursions allow a correction to be made for non-pyroelectric background currents.

Description of Apparatus

The apparatus used for the continuous measurement of the alternating pyroelectric current during thermal depolarization is illustrated in Figure 1.

The sample is located in a copper cell with a pyrex window, and the cell is immersed in an oil bath contained by a clear glass Dewar flask. The internal dimensions of the cell were designed to be only slightly larger than those of the hoop-mounted sample in order to keep the thermal mass small. The interior of the cell normally contains exchange gas admitted through a thin-wall stainless steel tube extending above the surface of the oil bath. The time constant for thermal equilibration of the sample after immersion of the cell into a warm or cool bath is

around 20 seconds when air at atmospheric pressure is used as exchange gas. This thermal equilibration time is satisfactory for depolarization studies when the bath temperature is ramped at the rate of a few kelvin per minute in which case the sample temperature is not expected to lag the bath temperature by more than a few kelvin. The stainless tube is also used as a conduit for tetrafluoroethylene-insulated electrical wires. One pair of wires carries the pyroelectric current between the sample electrodes and a bench mounted current amplifier. Contact between the sample electrodes and the wires was established by contact rings and spring fingers painted over with a silver-filled, conductive rubber. A second pair of wires carries the thermal emf generated by a copper-constantan thermocouple placed inside the cell very close to the sample.

A heater operated by a microprocessor-driven, electronic controller/programmer heats the stirred oil bath at a constant rate which is usually chosen to be 5 kelvin per minute. The difference between the voltage of a thermocouple outside the cell and a linear voltage ramp is used as an error signal for the controller. The system is capable of heating the sample to its melting point at the programmed rate.

A 100-watt arc lamp, lens, and rotary chopper are used to heat the sample radiatively and periodically at a frequency of around 10 Hz. Since the diffusivity controlled thermal time constant of 25 μm thick PVF_2 is around 1 ms [23], the periodic temperature changes of the sample can be regarded as uniform across the thickness.

The signal from the current amplifier is sent to a 2-Hz (between -3 dB points) band pass filter which is tuned to the 10 Hz frequency of the mechanical chopper and then to an ac to dc converter and a recorder. The recorded data consisted of simultaneous records of the pyroelectric response and of the voltage of the thermocouple. In all the present

measurements, a nonpyroelectric dc current was present. This dc current which normally would be measured in TSC experiments was large enough when uncompensated to drive the current amplifier to saturation due to the finite, though short, time constant of its input circuit which includes a measuring and range-setting resistor. Most of this dc current was cancelled by using the front-panel suppression control built into our current amplifier, but the suppression was effective in preventing amplifier overload only if the amplifier was set at one of its relatively insensitive ranges (to minimize the input time constant) or if the sample temperature was swept at a rate slower than 5 K/min.

Results

Table I shows the room-temperature pyroelectric coefficients of the hoop-mounted samples prior to the depolarization runs. The listed values which cover an order of magnitude range of pyroelectric activity were obtained assuming that the active area was that of the circular electrodes with the tabs excluded. Experience has shown that this assumption tends to yield somewhat larger coefficients than are obtained from the disk samples cut from the electroded area. Nevertheless, larger values in Table I are representative of well poled samples. A large dependence on T_p is found in the pyroelectric activity of the samples poled at $E_p = 1$ MV/cm. Similarly, a large dependence on E_p is found in the pyroelectric activity of the samples poled at room temperature. These trends are consistent with previous observations [24-26].

Figure 2 shows the rms amplitude of the 10 Hz pyroelectric currents normalized (arbitrarily) to the amplitude at 40 °C as a function of temperature for the PVF₂ samples poled at $E_p = 1$ MV/cm at various T_p . Figure 3 shows similar results for samples poled at or near room temperature at various E_p . In both figures, the temperature was raised at the

rate of 5 K/min. The above results suggest that the form of the curves varies more with the poling temperature T_p than with the poling field E_p or the initial pyroelectric activity.

Discussion

To understand the pyroelectric response curves in Figs. 2 and 3 we need to understand the source of the pyroelectricity. A molecular dipole theory of pyroelectricity in PVDF [7] leads to the following expression for the pyroelectric coefficient

$$p_y = \alpha P_0 (1 + A + B)$$

where A and B involve parameters arising from electrostriction and dipole fluctuations and amount to about 0.5 each in the above expression, $\alpha = d \ln l_g / dT$ is the temperature coefficient of the sample thickness, l_g , and $P_0 = \phi P_x \langle \cos \theta \rangle$ is the sample polarization. The latter is the product of three factors: the polarization, P_x , of the polar crystals, the volume fraction, ϕ , of the polar crystals, and an orientation factor $\langle \cos \theta \rangle$ in terms of the average angle, θ , between the vector \vec{P}_x , which has a distribution of orientations among polar crystals, and the vector \vec{P}_0 , which is normal to the surface of the film. The non-crystalline fraction is in a supercooled liquid phase. Neither this phase nor any other non polar crystal phase, contributes to P_0 ; but, both affect α and hence the temperature dependence of the pyroelectric response. For a reasonable dynamic model (quasi-harmonic librations, etc.) the terms A and B vary by no more than 10% between room temperature and the melting temperature. Therefore, over a wide range of temperature, the temperature dependence of p_y is expected to be due primarily to the compounded temperature dependences of α and P_0 . The thermal coefficient α is expected to increase smoothly with temperature based on specific volume data on related samples [27,28], and on x-ray data [28] which measure the

expansion of the crystalline components only. In general, we expect α to increase both because of the anharmonicity of molecular and inter-molecular vibrations and because of the volume increases associated with the progressive melting of crystals. Semicrystalline polymers like PVF₂ typically melt over a 50-100 °C temperature range, and the specific volume of the melt is 10-15% greater than that of the crystal [29]. The sample polarization P_0 may decrease with temperature because of both crystal melting (decrease in ϕ) and irreversible loss of orientation of the crystal polarization (decrease in $\langle \cos\theta \rangle$) without melting. In the temperature scanning studies referred to earlier [10,11], the measurement of two piezoelectric moduli in one case [10] or a piezoelectric and a mechanical modulus in the other case [11] allowed the authors to conclude that decreases of piezoelectric activity with increasing temperature beginning around 80 °C were due to loss of polarization rather than to effects of mechanical modulus changes.

Analogously, we propose here that the decreases of pyroelectric activity with increasing temperature in our measurements are due to loss of polarization rather than to thermal expansion effects. While we did not separately measure the temperature dependence of α and of P_0 , we obtained some insight on their separate contributions by measuring the pyroelectric response of a sample taken through a series of temperature cycles beginning and ending at room temperature but extending to successively higher temperatures. The result for a sample poled at 1 MV/cm and at 109 °C is shown in Fig. 4. Several features of Fig. 4 are of interest. In the first two cycles, where the maximum temperature does not exceed 69 °C, the response during cooling practically retraces the response during heating. This essentially reversible behavior indicates no net loss of P_0 below 69 °C. In the third cycle, where the maximum temperature first extends to 79 °C, and in subsequent cycles where the temperature extends respectively to 109,

125, 150 °C, the response during the cooling part of each cycle lies below the response during the heating part. This indicates an irreversible loss of P_0 in those cycles. Finally, at all temperatures studied, the response during the heating part of any cycle practically retraces the response during the cooling part of the previous cycle until the temperature reaches the highest previously attained temperature. This behavior indicates that the irreversible loss of P_0 occurs immediately after the sample is first brought to a temperature above 69 °C. This implies that during cooling and subsequent reheating up to the previous maximum temperature, P_0 is essentially constant and the observed temperature dependence must be essentially that of α . To test this contention, we plotted the reheating parts of the curves in Fig. 4 normalized so as to have the same value at 40 °C. The results are shown in Fig. 5. These normalized curves have very similar temperature dependences although they are not superimposed as they should be if $\alpha(T)$ were strictly reproducible with repeated heating and cooling. For reference we have plotted also on Fig. 5 normalized thermal expansion data obtained by rough graphical means from the specific volume curve obtained by Nakagawa and Ishida [28] on α -phase samples. Finally, we have plotted in Fig. 6, the pyroelectric activity remaining at 40 °C after each successive temperature cycle as a function of the maximum temperature reached in each cycle. The remaining pyroelectric activity is constant up to approximately 70 °C, and then decreases to zero at a temperature consistent with complete melting of the crystal phases. Explanations for the apparent thermal stability of P_0 up to ~ 70 °C and for its roughly linear decrease above ~ 100 °C are currently being pursued.

In light of the above discussion, we can reexamine the results of Figs. 2 and 3. For ease of comparison in this discussion, we show in Figs. 7 and 8 representative curves from Figs. 2 and 3. The data show

two main regions of irreversible loss of activity (i.e., loss of P_O), one just above 60 °C and one near the maximum melting temperature starting around 140 °C. An additional loss at intermediate temperature seems to exist for samples poled at 109 °C. The source of the 60 °C loss is not presently known. The loss above 140 °C is consistent with melting of the polar crystals. The intermediate loss seems to coincide with the poling temperature for the 109 °C poling temperature case. But, no similar loss feature is observed for the other poling temperatures. After poling at 1 MV/cm (Fig. 7), note that, with the exception of the sample poled at 109 °C, the lower the poling temperature the better a sample retains its activity at high temperatures. Note also that the sample poled at the highest temperature of 109 °C performs better at lower temperatures in terms of retention of activity. Figure 8 reveals that there is not as strong a dependence of sample stability on poling field for samples poled at 29 °C. However, the apparent change of pattern in Fig. 7 between 83 °C and 109 °C, and the apparently deviant behavior of the 2 MV curve in Fig. 8 preclude making strong generalizations.

In some applications, the relative change in activity at some elevated temperature may not be as important as the remaining absolute activity. We illustrate this point in Fig. 9 where selected response curves have been scaled according to the measured pyroelectric coefficients from Table I. In this Figure, we see data for two well poled samples, one having been poled at 109 °C with 1 MV/cm, the other at room temperature with 2.8 MV/cm. Both samples have roughly the same pyroelectric activity at room temperature initially. It is apparent that the sample poled at high temperature retains more activity up to just above 100 °C (roughly the poling temperature) and that the sample poled at room temperature retains significantly more activity above approximately 110 °C.

Summary and Conclusions

The present work demonstrates that processing variables (the poling temperature in particular) may affect rather strongly the relative thermal stability of the pyroelectric activity at various temperatures. We have shown that two samples initially of equal room-temperature activity - one poled at ambient temperature with a high field, the other poled at high temperature (approx. 110 °C) with a weaker field, both in the same poling time - have markedly different thermal stability properties when thermally depolarized. The sample poled at ambient temperature retains more of its pyroelectric activity above 110 °C (say at 140 °C) than does the sample poled at high temperature. Measurements similar to those presented here where other processing variables (mechanical, thermal, electrical and temporal) are varied systematically should provide valuable information about the relationship between thermal performance and processing conditions.

Furthermore, measurements on single phase and mixed phase samples using the techniques developed here, should give insight on the temperature dependence of the polarization and on the depolarization mechanism.

The present measurement method provides quick data on the short-term retention characteristics of the pyroelectric activity over a wide range of temperature. The information obtained about loss of polarization is similar to that obtained from related piezoelectric measurements [10,11]. The present data should be complementary to long term isothermal aging data which are more time consuming to obtain. The connection between short and long term aging data needs to be established better. This we intend to do in future work.

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Table I
Pyroelectric Coefficients of Samples Mounted in Hoops

<u>Sample No.*</u>	<u>T_p (°C)</u>	<u>E_p (MV/cm)</u>	<u>P_y (nC/cm²/K)</u>
1	103	1	3.57
2a	103	1	3.54
2b	103	1	3.57
3	83	1	2.77
4a	83	1	3.17
4b	83	1	3.06
5a	57	1	2.11
5b	57	1	1.95
6a	57	1	2.09
6b	57	1	2.10
7a	29	1	0.37
7b	29	1	0.49
8	24	1.6	2.26
9	24	2	2.58
10a	24	2.8	3.84
10b	24	2.8	N/A
11	24	2.8	N/A

*Samples bearing the same numeral (e.g. 2a, 2b) were poled together.

Figure Captions

- Fig. 1 Schematic of apparatus
- Fig. 2 Relative pyroelectric response vs. temperature of PVF₂ samples poled for 10 minutes with a 1MV/cm poling field at various maximum poling temperatures, T_p. For all curves, the temperature was increased at a constant rate of 5 K/min. Curves which are normalized to unity at 40 °C are offset vertically for clarity. Numbers on curves identify samples in Table I.
- Fig. 3 Relative pyroelectric response vs. temperature of PVF₂ samples poled for 10 minutes at room temperature with various poling fields, E₀. For all curves, the temperature was increased at a constant rate of 5 K/min. Curves which are normalized to unity at 40 °C are offset vertically for clarity. Number on curves identify samples in Table I.
- Fig. 4 Relative pyroelectric response vs. temperature of a PVF₂ sample which was poled for 10 minutes at 109 °C with 1MV/cm, as the temperature is increased and decreased in cycles extending to progressively higher maximum temperatures. The maximum cycle temperatures are denoted by T₁, T₂, etc.
- Fig. 5 Reheating parts of cycles in Fig. 4 normalized to a common value at 24 °C. As discussed in text, the curves are believed to represent $\alpha(T)$. The dashed curve was calculated from volumetric data on α -PVF₂ [28].
- Fig. 6 Remanent response after each cycle vs. maximum cycle temperature. As discussed in text, the curve is believed to represent $\phi P_0(T) \langle \cos \theta \rangle$
- Fig. 7 Relative pyroelectric response of representative PVF₂ samples poled for 10 minutes, with 1MV/cm, at various maximum poling temperatures, T_p.
- Fig. 8 Relative pyroelectric response of representative PVF₂ samples poled for 10 minutes, at room temperature, with various poling fields.
- Fig. 9 Absolute pyroelectric response of selected PVF₂ samples from Fig. 1 using different combinations of poling temperature and poling field for the same poling time of 10 minutes. Poling variables are shown in parentheses on curves.

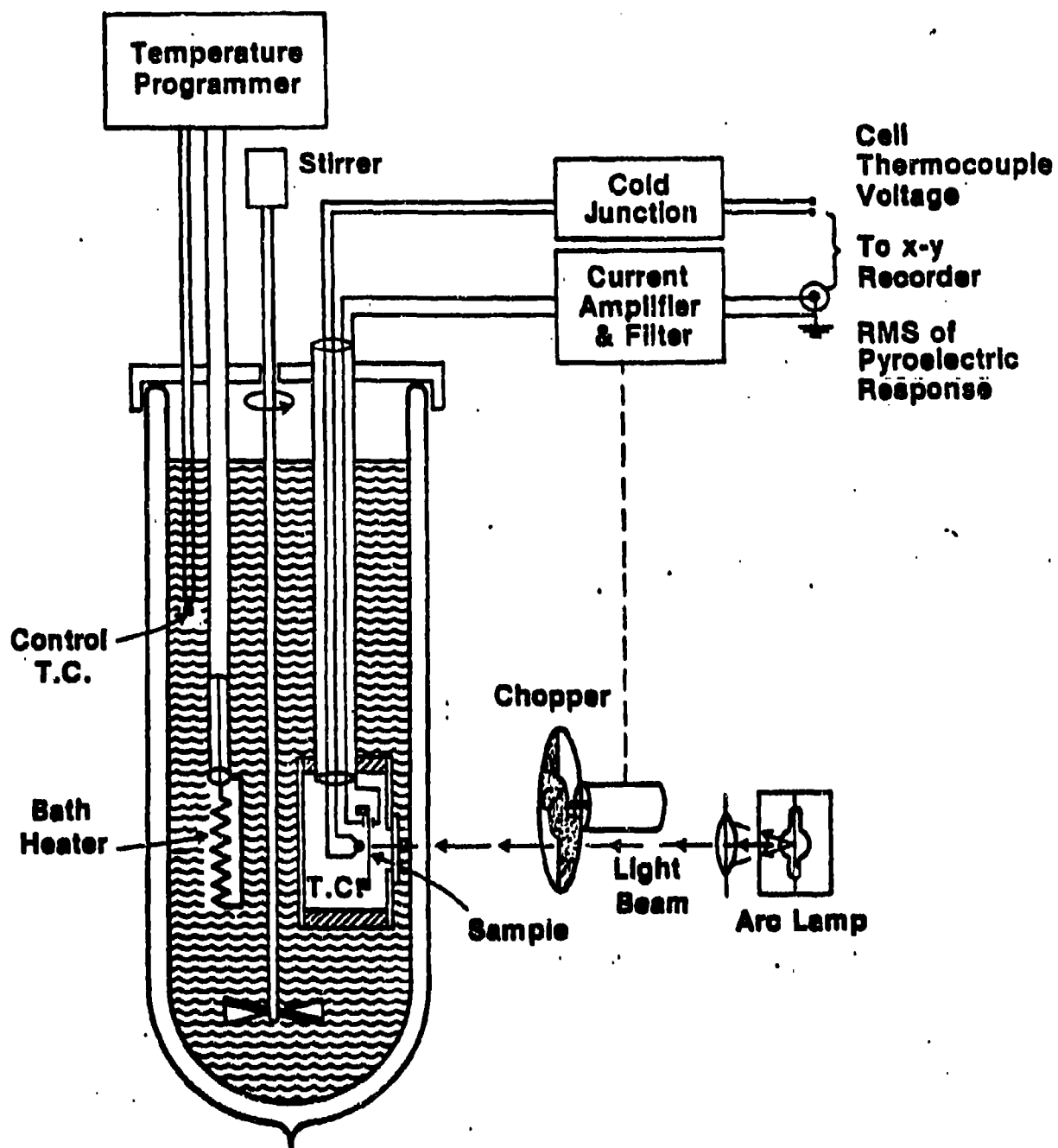


Fig. 1

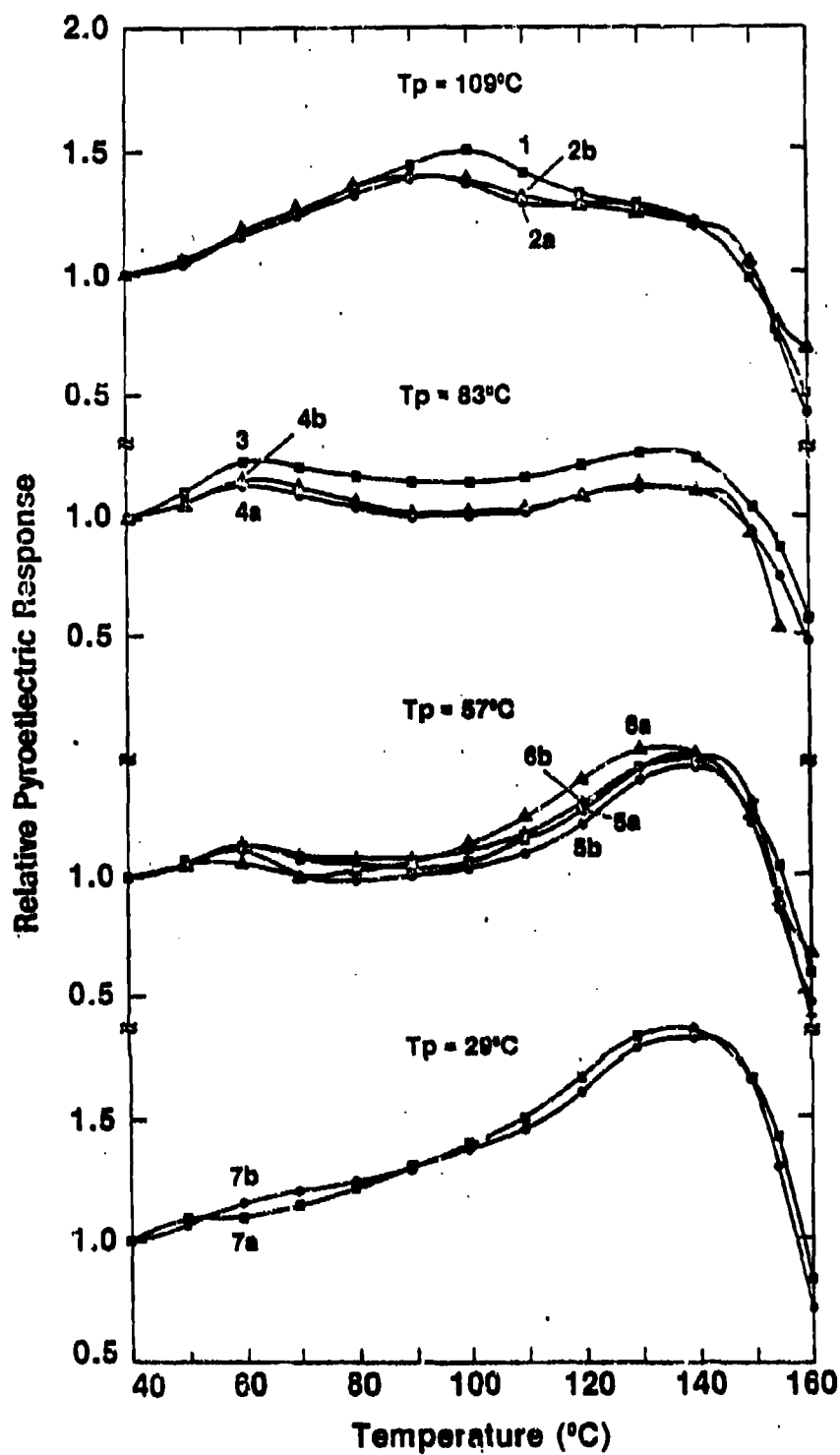


Fig. 2

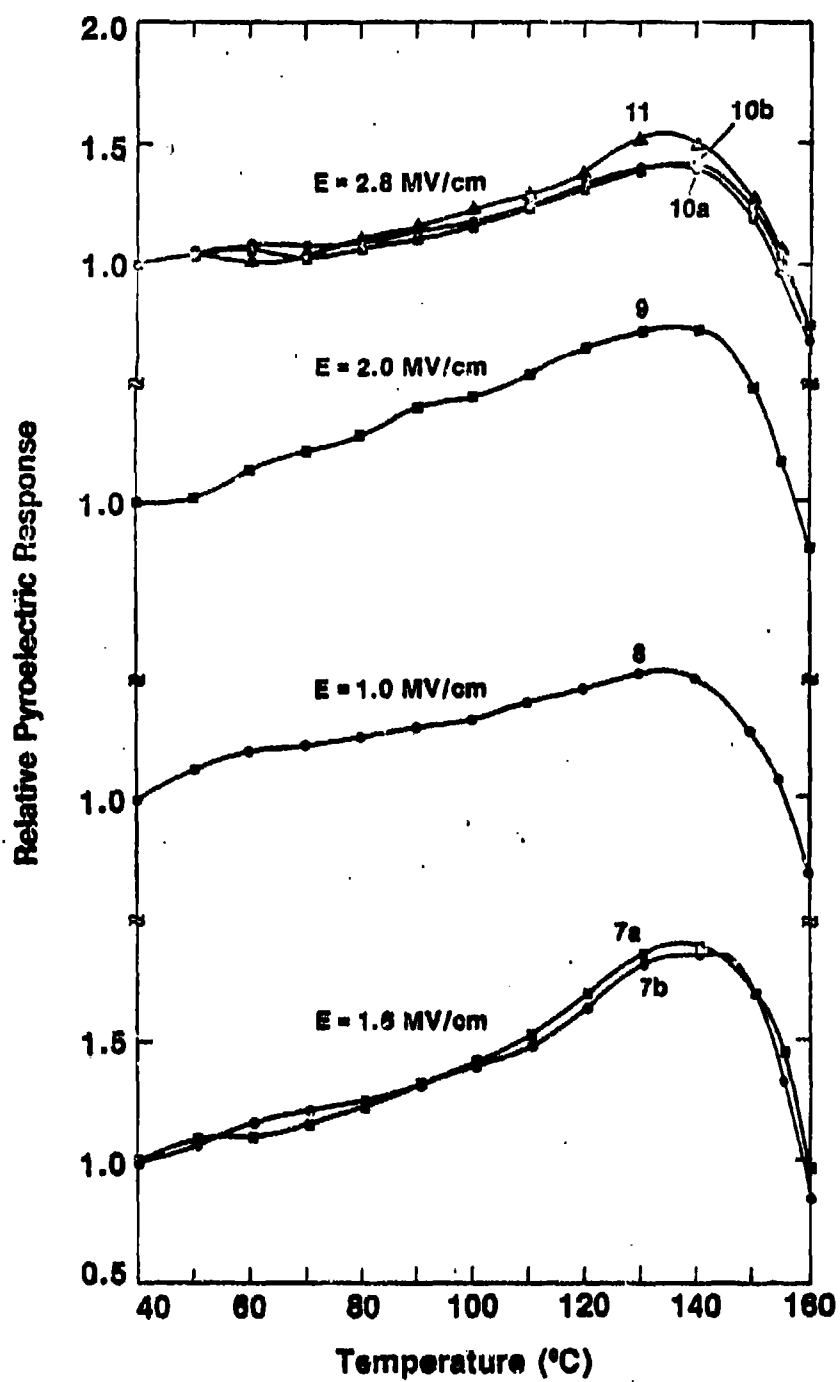


Fig. 3

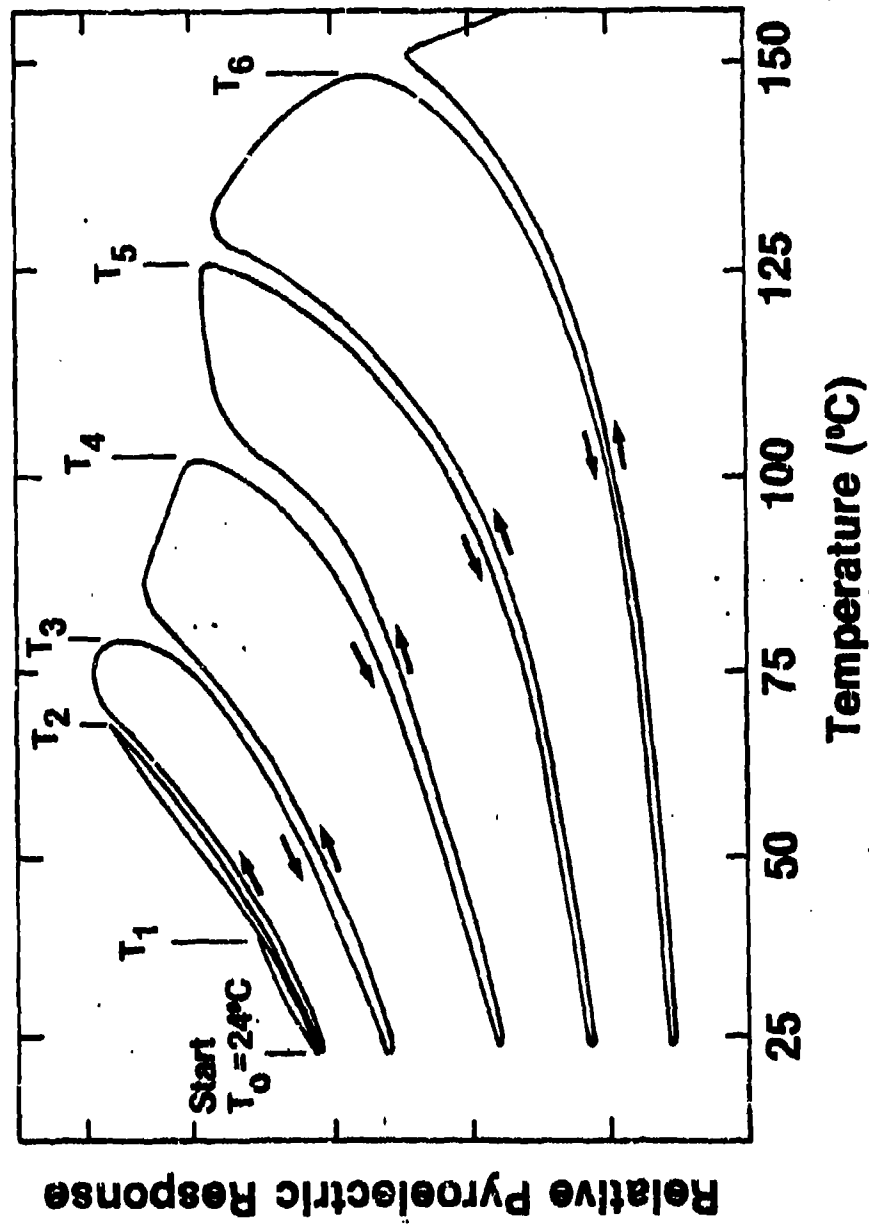


Fig. 4

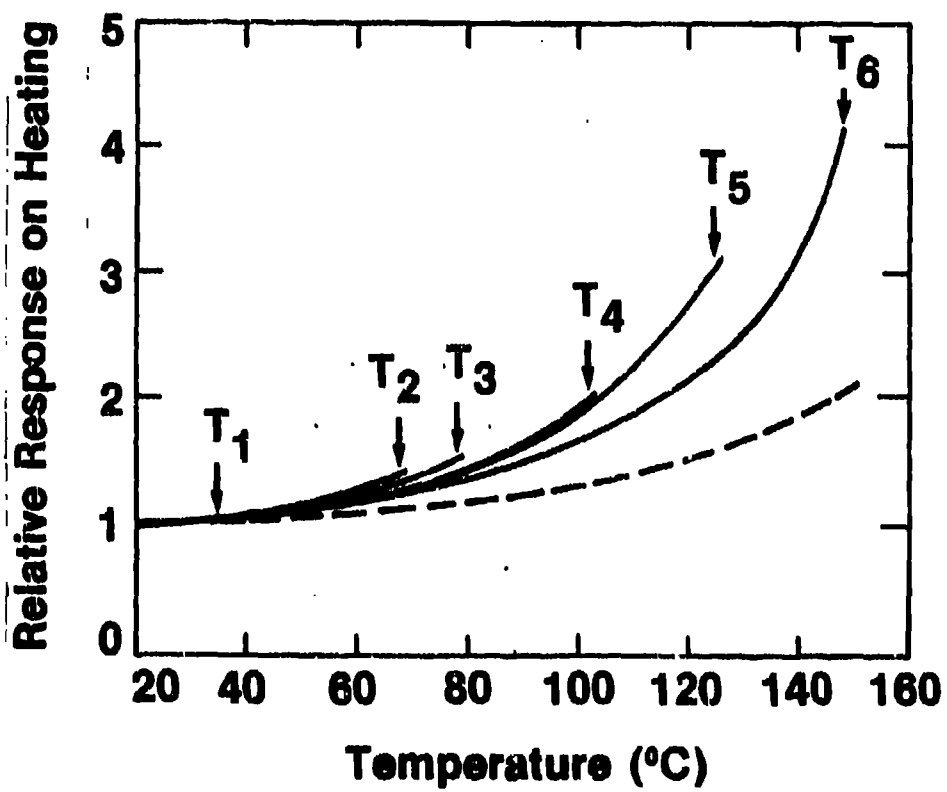


Fig. 5

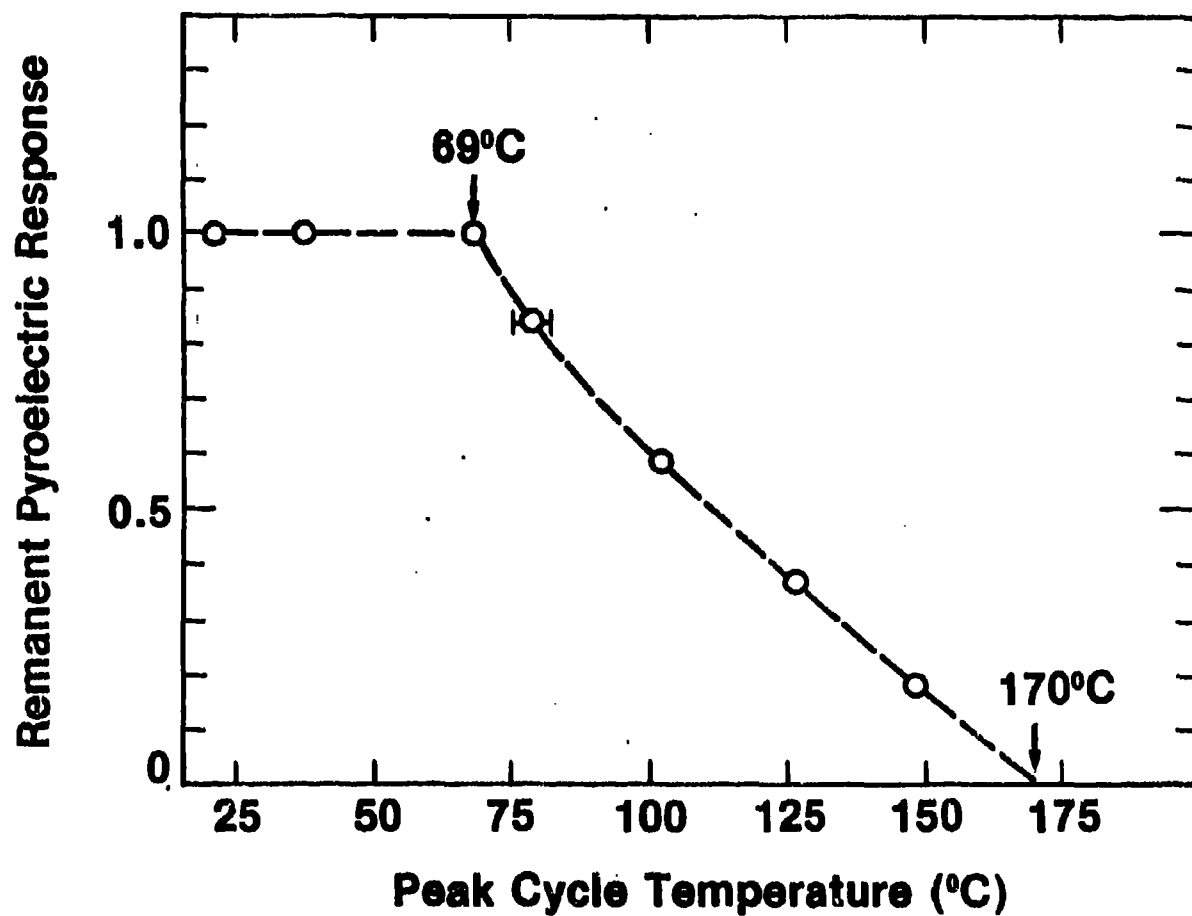


Fig. 6

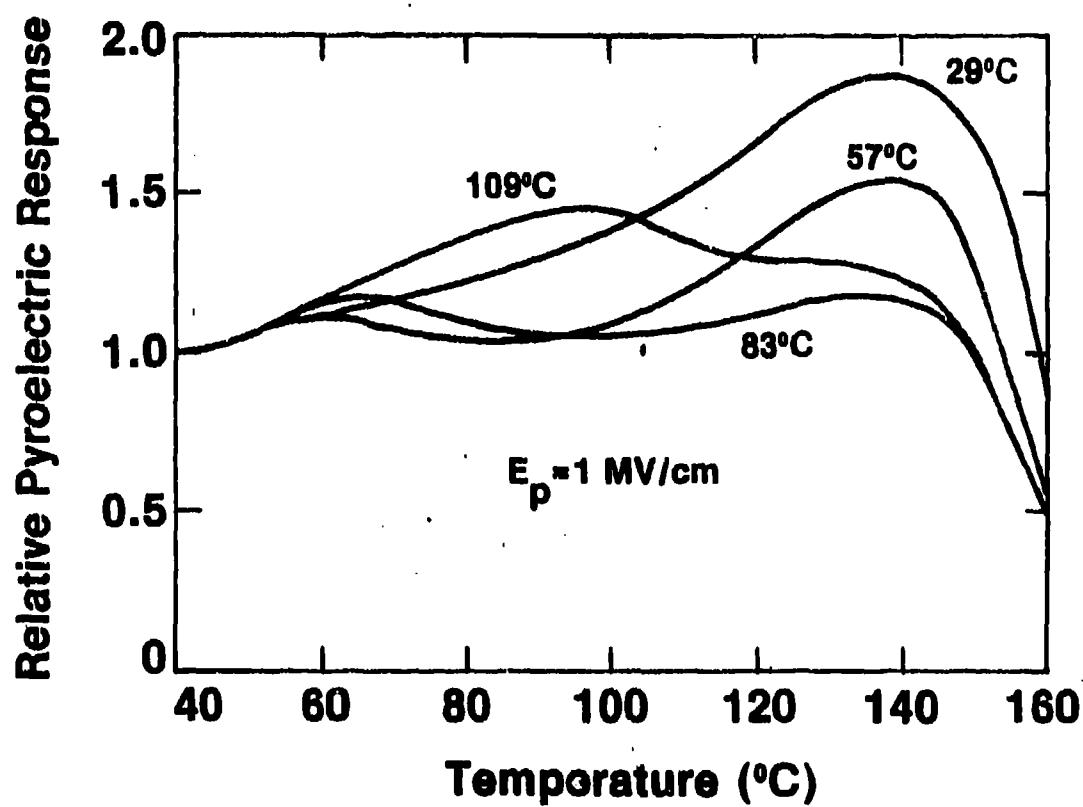


Fig. 7

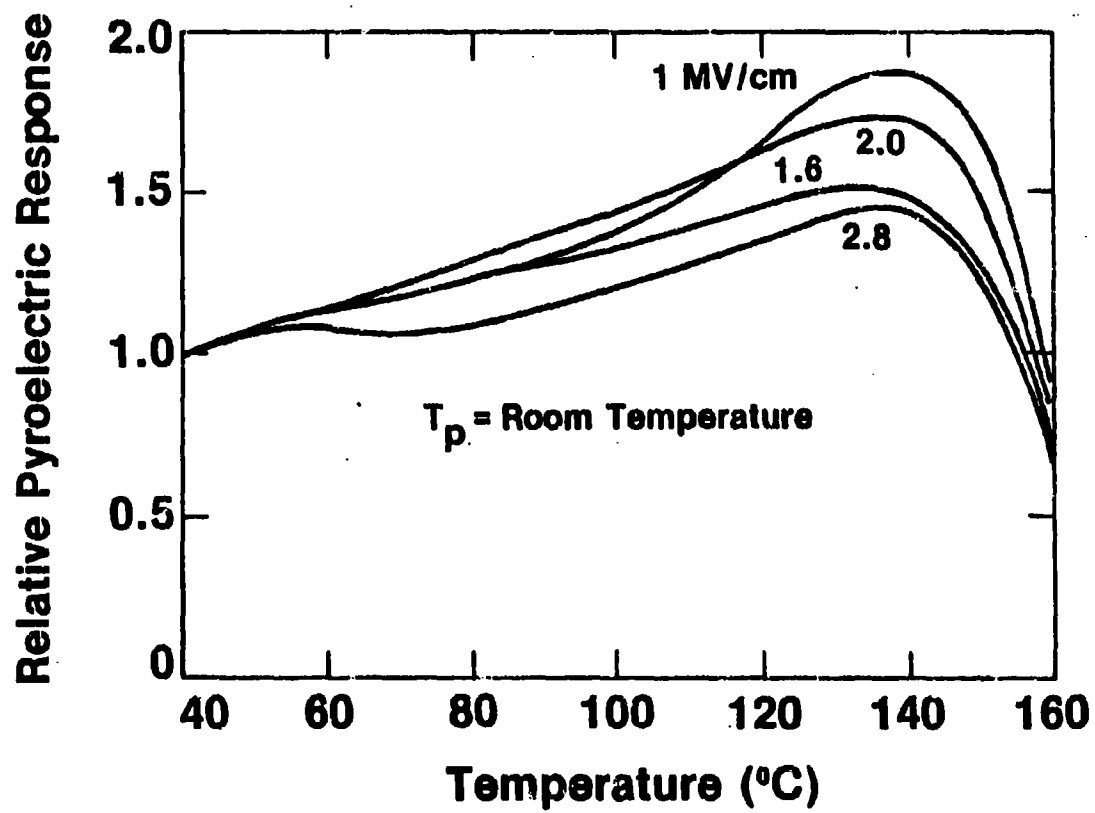


Fig. 8

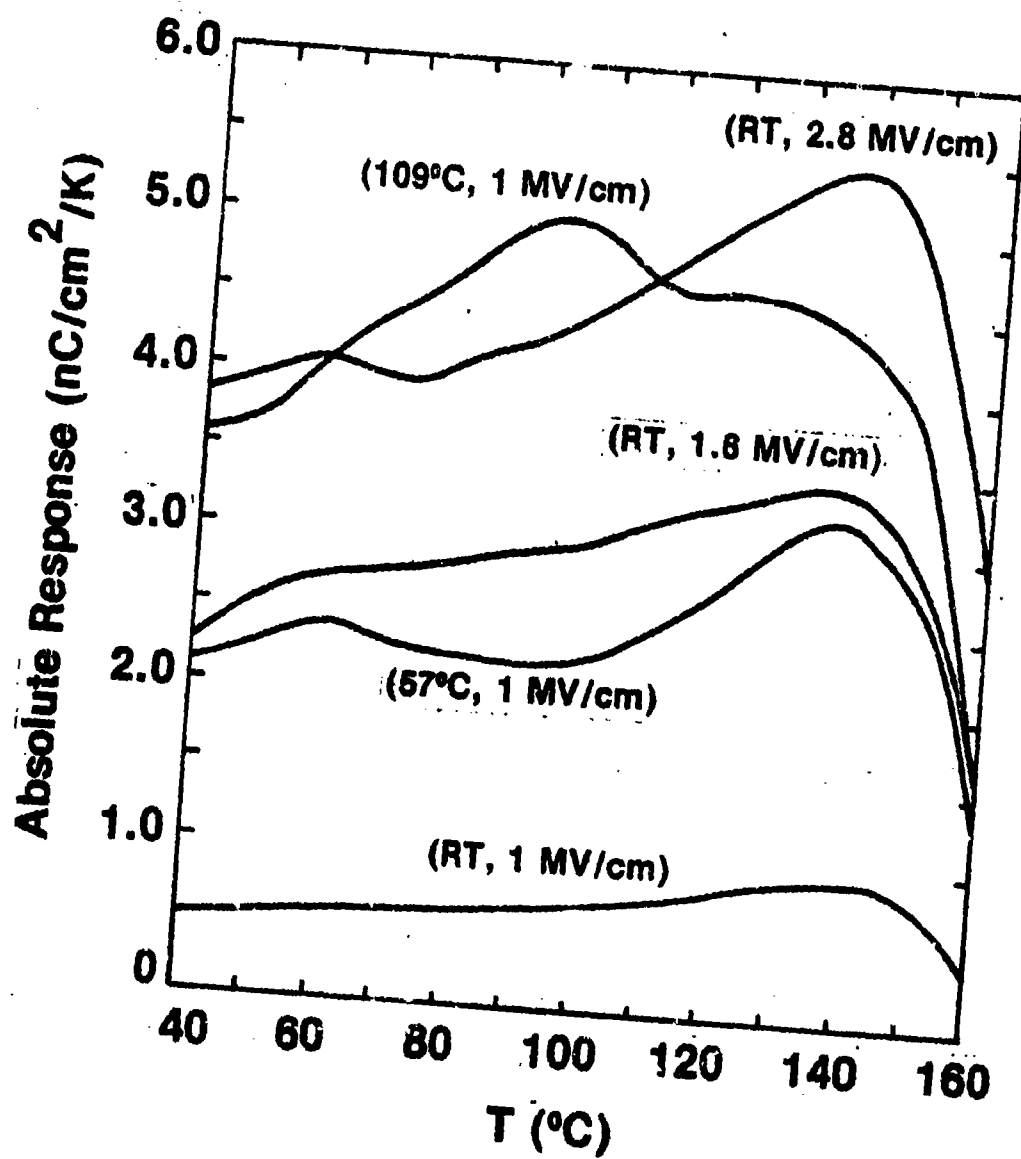


Fig. 7

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